

Structure of Boron Nitride Nanotubes: Tube Closing Vs. Chirality

Madhu Menon*

Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055

and

Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045

Deepak Srivastava**

Computational Nanotechnology at NAS Systems Division

NASA Ames Research Center, MRJ, Mail Stop T27-A1, Moffett Field, CA 94035-1000

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Abstract

The structure of boron nitride nanotubes is investigated using a generalized tight-binding molecular dynamics method. It is shown that dynamic relaxation results in a wavelike or "rippled" surface in which the B atoms rotate inward and the N atoms move outward, reminiscent of the surface relaxation of the III-V semiconductors. More importantly, the three different morphologies of the tube closing with flat, conical and amorphous ends, as observed in experiments, are shown to be directly related to the tube chiralities. The abundance of flat end tubes observed in experiments is, thus, shown to be an indication of the greater stability of "zig-zag" BN tubes over the "arm-chair" tubes under experimental conditions.

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I. INTRODUCTION

The discovery of carbon nanotubes by Iijima, [1] has set off a tremendous explosion in general interest in these quasi one-dimensional structures. Most carbon nanotubes observed tend to be multi-walled with spacing between the walls close to inter-planar distance in graphite. Single-walled nanotubes (SWN) are also increasingly produced and observed in transmission electron microscopy (TEM) measurements. The SWN nanotubes consist of rolled-up graphene sheets with various chiralities. The electronic structure of these tubes can be either metallic or semiconducting, depending on both the diameter and chirality which can be uniquely determined by the chiral vector (n, m) , where n and m are integers. [2-6] More recently, TEM measurements have revealed bends in carbon nanotubes that were attributed to the presence of pentagon-heptagon defect pairs in an otherwise perfect hexagonal arrangement.

The possibility of existence of tubular structures made of non-carbon elements has also received much attention lately. In particular, tubules made up of boron nitride have been the subject of recent investigations, both theoretically and experimentally. [7-12] Successful synthesis of pure boron nitride nanotubes by arc discharge between a BN-packed tungsten anode and a copper cathode has been reported recently. [11] An alternate method to produce pure BN nanotubes using arc-discharged hafnium-diboride electrodes has been the subject of a more recent experimental work. [12] This method yields large quantities of reduced number of layers, including single-wall tubes. Furthermore, electron-energy-loss spectroscopy yields a B/N ratio of approximately 1. A very curious feature of these tubes is the structure of the tube ends. Majority of the tubes observed in experiment have a very characteristic end with a flat tip. [12] A smaller fraction of the tubes show cone-like termination and some show ends made up of amorphous-like material. [12] We note that carbon nanotubes almost always show fullerene caps at their ends when they close.

Theoretical investigations of the structure of BN nanotubes have relied on the similarities between carbon and BN-based materials. Determination of the precise geometry requires

use of molecular dynamics methods that enable full symmetry unconstrained energy minimization. Because of the lack of tight-binding total energy schemes for BN systems, most of the calculations were restricted to tubes with geometries identical to those formed by carbon, ie., with all atoms at the same distance from the symmetry axis. [7] More recently, total energy minimization based on the density functional theory (DFT) within the local density approximation (LDA) have been performed which indicated a buckling of the B-N bond. [8]

In this work we perform molecular dynamics simulations on BN nanotubes to determine its precise structure. The theoretical method used in the present work is the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy [6,13] that allows for full relaxation of covalent systems with no symmetry constraints. The GTBMD scheme makes explicit use of the nonorthogonality of the orbitals resulting in sufficient local coordination information in the electronic energy term. As a result, only a minimal number of adjustable parameters (only 4 for each chemical species) are required for obtaining a transferable scheme that works well in the range all the way from a few atoms to the bulk solid. Successful applications of the GTBMD method to Si and C systems have been reported elsewhere. [6,13,14] The extension of the GTBMD to treat interactions in heteroatomic systems involves averaging of the adjustable parameters. [15] This is made easier by the fact that the functional form is taken to be the same for all species within the GTBMD scheme.

The GTBMD relaxation of an 136 atom hexagonal BN cluster yielded an average B-N bond length of 1.42 Å for the three-fold coordinated atoms, in very good agreement with the accepted value of 1.42 Å. [16] When B and N atoms arrange themselves to form tetrahedrally coordinated cubic-BN, the GTBMD gives a B-N bond length of 1.51, comparing favorably with the experimental value of 1.57 Å. [16] Furthermore, for an isolated BN dimer, the B-N bond length is found to be 1.24 Å, in very good agreement with the experimental value of 1.28 Å. [17] Thus, the present scheme gives B-N bond lengths in two, three and four-fold coordinated structures of BN in very good agreement with experiment.

The GTBMD relaxation was performed on three BN nanotubes, each with a B/N ratio of 1. They are: (I) A (10,0) “zig-zag” tube, (II) (5,5) “arm-chair” tube and, (III) a (8,2) “chiral” nanotube. The index notations are taken from reference. [18] These systems were selected because they represent all three distinct types of nanotubes. Unlike carbon nanotubes, all BN nanotubes are large gap semiconductors, [8] as is the graphitic BN sheet. The starting configurations had the “perfect” geometry that is typical of carbon nanotubes. The symmetry unconstrained relaxation results in a wavelike or “rippled” surface in which the B atoms rotate inward to an approximately planar configuration, whereas the N atoms move outward into a corresponding pyramidal configuration. Additionally, some of these tubes show reconstructions at the open ends. The relaxed BN nanotubes are shown in Figs. 1 and 2. As shown in these figures, the B atoms and N atoms arrange themselves in two concentric cylinders with all B atoms occupying the inner cylinder and all N atoms occupying the outer cylinder.

This surface buckling must be understood on general grounds by a consideration of the special nature of the chemical bonding on the surfaces of III-V semiconductors. It is generally agreed that dangling bonds of the sp^3 type are unstable on the surface of III-V compound semiconductors. [19] In order to lower surface electronic energy, the orbitals of the surface atoms rehybridize to form three planar sp^2 -type bonds plus an empty dangling hybrid on the group III species. The rehybridization lowers the energy of the doubly occupied dangling states of the group V atoms while raising the energy of the empty dangling states of group III atoms, making the buckling process energetically favorable. The three major types of III-V semiconductor surface planes are those of (100), (110), and (111) symmetry. Of these three types, only (110) planes are non-polar. The buckling of the BN nanotubes resemble more closely to those of the (110) surfaces of the III-V semiconductors.

Although the same type of reconstruction is observed in tubes I, II and III, the bond length analysis reveals some subtle distinguishing features. The alternate inward-outward displacements of the atoms in tube I (“zig-zag”) results only in simple rotation of the bonds with no change in the bond lengths when compared to the relaxed planar graphitic BN

sheet. Tubes II and III (“arm-chair” and “chiral”, respectively), on the other hand, show a slight increase in the average B-N bond lengths on relaxation (1.43 Å) when compared with the relaxed graphitic BN sheet. This can be explained by the effects of relaxation on the chirality. In the “zig-zag” tube (I), many of the B-N bonds are parallel to the tube axis. The rotational relaxation, therefore, is facilitated with least effect on the diameter of the tube causing minimum strain. In the “arm-chair” tube (II), however, many of the B-N bonds are perpendicular to the tube axis and along the circumference. A rigid rotational relaxation, therefore, will force a decrease in the diameter causing strain that will strongly depend on the diameter. Shorter the diameter, larger the strain on relaxation. Some of this strain can be relieved by an increase in the B-N bond length which explains the slight increase in the bond lengths on relaxation. Similarly, the “chiral” tubes can also experience strain due to the effects of relaxation.

II. TOPOLOGICAL DEFECTS, TUBE CLOSING AND CHIRALITY

Another area where the distinct chemistry of the BN nanotube manifests itself is at the closing of the free tube ends. The closing involves change in the diameter. In the case of carbon nanotubes the closure is mostly through the formation of fullerene caps which contain pentagons in addition to the hexagons. The change in diameter, however, is generally achieved through the introduction of a pentagon-heptagon pair, positioned adjacent to each other. [20] Presence of pentagons or heptagons in BN nanotubes, however, introduces energetically unfavorable B-B or N-N bonds that destabilize the structure. A different mechanism, therefore, must be responsible for stable tube closing. Interestingly, recent experimental results on BN nanotubes using high resolution TEM imaging show very characteristic ends with flat or conical tips and some samples showing amorphous-like material at the tip. [12]

It is clear that the closure of BN nanotubes must be accomplished through the formation of only even numbered topological defect rings to avoid formation of unfavorable B-B or

N-N bonds. The junction of BN nanotubes must also be accomplished through only even numbered topological defect rings. Indeed, in our molecular dynamics simulations, attempts to change diameter through the introduction of heptagon-pentagon pairs resulted in the breaking of several of the B-B and N-N bonds on relaxation showing that this mechanism cannot be responsible for tube closing. Bending or change in the diameter in “zig-zag” tubes can be readily achieved through the introduction of hexagon-square pairs. In Fig. 3 a we show a fully relaxed tip of a (12,0) BN nanotube with bending achieved via three hexagon-square pairs. [12] Unlike the heptagon-pentagon pair, the hexagon-square pair has two fewer atoms resulting in sharp curvature and abrupt tube closing as seen in Fig. 3a. Although the flat end shown in Fig. 3a corresponds to a triangular facet (three 120° disclinations), higher order facets are also possible with squares at each corner.

Since the hexagon-square pairs give rise to flat ends, another mechanism has to be invoked for the pointed conical (“pencil-like”) tube closing observed in many of the BN nanotube samples. [12] Such a closing must be achieved through a more gradual decrease in the diameter. We propose that this can be accomplished by introducing adjacent octagon-square pairs shown in Fig. 3b. An example of the octagon-square pair defect at the conical end of an arm-chair tube is indicated by an arrow in the figure. These pairs contain the same number of atoms as heptagon-pentagon pairs. The tube shown in the figure is an GTBMD relaxed (5,5) “arm-chair” tube. A more gradual formation of the conical tip can be achieved similarly by gradual insertions of the octagon-square pairs in an otherwise all hexagonal lattice. The octagons are energetically much more stable than heptagons due to the lack of B-B or N-N bonds. Since the octagon-square pairs must be oriented along the tube axis for achieving the conical shape, the most likely “host” tube for such a cap must be an “arm-chair” tube (Fig. 3b).

The “chiral” tubes, on the other hand, cannot accommodate either hexagon-square or octagon-square pairs and are forced to have unfavorable pentagons and, possibly, heptagons while attempting to close. As we found in our molecular dynamics simulations of the chiral (8,2) tube, this results in the breaking up of B-B and N-N bonds with reactive dangling bonds

that can disrupt the smooth tube closing by forming higher coordinated structures. This may explain the formation of amorphous-like structures found at the ends of BN nanotubes in many cases.

This raises an important issue regarding the connection between the experimentally observed tube closing vs. chirality. The fact that flat ends are seen in experiment more abundantly than conical ends may indicate more abundant production of “zig-zag” tubes when compared with “arm-chair” tubes. This is in striking contrast to the case of carbon nanotubes where the experimental results supported by theory, so far, indicate preponderance of “arm-chair” nanotubes. [21] Recent experiments correlating chirality of a carbon tube with the conductance indicate that this might not be the case even for carbon nanotubes. [22] As shown in this work, the BN nanotubes, unlike the carbon nanotubes, show considerable reconstruction characterized by rotational relaxation on the tube surface. For the “zig-zag” tubes the resulting bond contraction/stretching is along the tube axis and, therefore, strain accommodation is easier because no appreciable force is created along the circumference. Similar reconstruction in the “arm-chair” tubes, however, results in the creation of forces along the circumference, requiring more strain accommodation in the structure. As calculated by us, some of the strain can be relieved by a slight increase in the overall B-N bond lengths. This gives further support to the stability of “zig-zag” tubes over the “arm-chair” tubes.

At the time of writing this manuscript we became aware of a recent paper [23] describing B-B and N-N bond frustration effects during the growth of BN nanotubes. There are significant similarities and differences between the two works. First, the significant similarity, through two different approaches, is in the observation that frustrated B-B and N-N bonds are not allowed, and hence odd membered rings are avoided in the growing edge [23] and in the final equilibrium structures as predicted in this work. The significant difference is in the final shape of the BN nanotube tips and their correlation with the structures of the nanotubes. We conclude that experimentally observed flat tips [12] are the closure of only zig-zag tubes with square-hexagon pairs. The “pencil-like” (conical) tapering of the tips are

due to the closure of only arm-chair tubes with octagon-square pairs. The relaxed chiral tube tips cannot avoid odd membered rings and end up with amorphous tips. The work of Blase et. al. [23] agrees with ours in that molecular dynamics relaxation for arm-chair tubes can result in the creation of a tip containing four squares and an octagon (Fig. 3) but makes no connection with all three shapes of the tips observed in the experiments. Focusing on pico second duration MD simulation of the growth they propose that the edges of the zigzag tubes are unstable and hence more arm chair tubes should be observed. The pico second duration MD simulations are limited only to the pico second duration kinetic processes and may not be a complete representation of the growth. The experimental observation of more flat tips [12] and the accommodation of larger bond rotation induced strain parallel to the tube axis, however, favor zig-zag over arm-chair tubes as proposed in this work.

In summary, we have presented our results of molecular dynamics simulations for BN nanotubes showing rotation relaxation, characteristic of surface reconstruction of III-V semiconductors. More interestingly, our simulations show that unlike carbon nanotubes, the chiralities of the BN nanotubes can be determined by observing the morphologies of tube closing. The geometries obtained using our simulations for flat and conical ends are in striking agreement with the TEM images reported. Furthermore, we have explained the preponderance of flat end zig-zag tubes in terms of the varying degrees of strains involved in the surface reconstruction among tubes with different chiralities.

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* e-mail: super250@convex.uky.edu

** e-mail: deepak@nas.nasa.gov

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FIGURES

FIG. 1. (a) Fully relaxed (10,0) “zig-zag” BN tube (I) with a B/N ratio of 1. The boron atoms are shown in dark circles and nitrogen atoms are shown in light circles. The surface appears “rippled”; caused by the inward displacement of the B atoms in conjunction with the outward movement of the N atoms. The surface relaxation is reminiscent of the (110) surface relaxation of the III-V semiconductors. The reconstruction is even more pronounced at the open ends.

FIG. 2. (a) Fully relaxed (a) (5,5) (II) and (b) (8,2) (III) BN tubes, also with a B/N ratio of 1.

FIG. 3. (a) Side and top view of the flat tip of (12,0) BN nanotube showing hexagon-square pairs. Nitrogen atoms are shown in red and boron in blue. (b) Side and top view of the “pencil-like” (conical) tube closing of the (5,5) “arm-chair” tube. The octagon-square pairs responsible for achieving gradual closing are aligned along the tube axis. The side view in is striking agreement with the TEM image reported in Ref. [12]

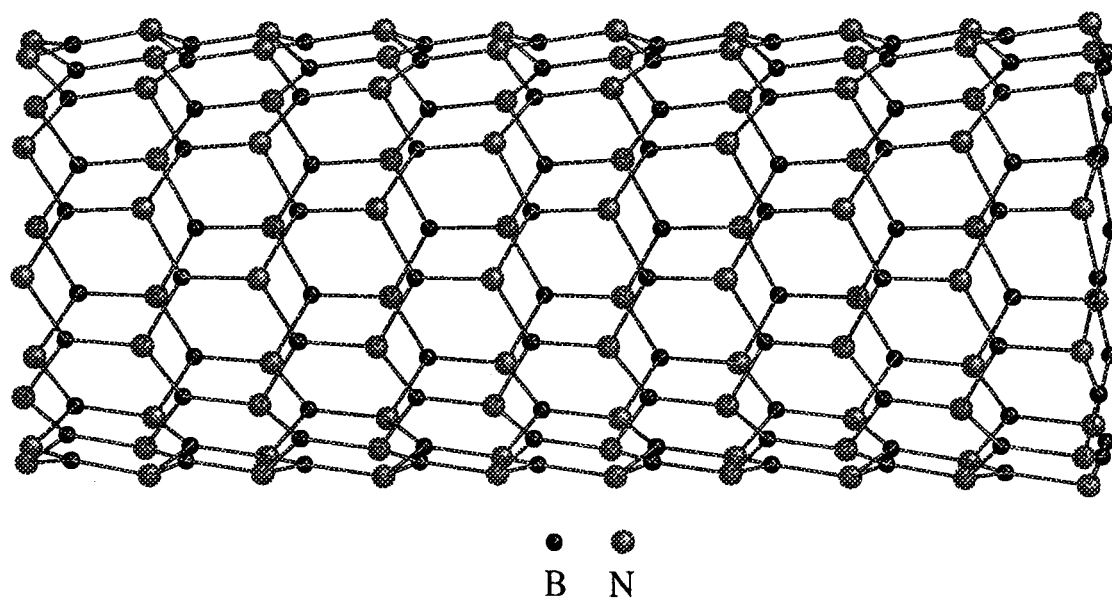
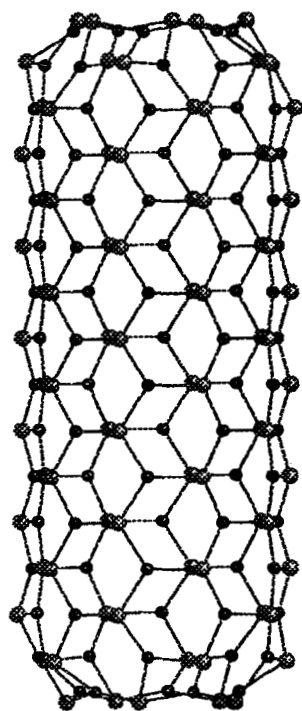
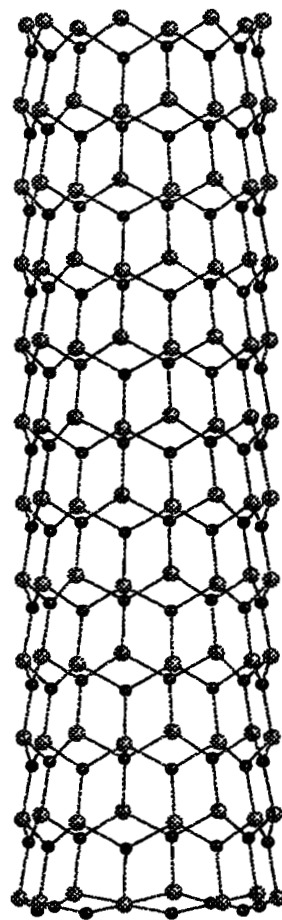


Fig. 1



(a)



(b)

